Science of the Total Environment 703 (2020) 135573

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Passive CO_2 removal in urban soils: Evidence from brownfield sites

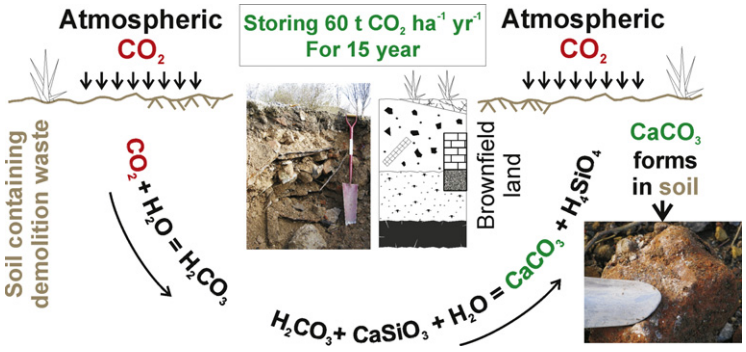
M. Ehsan Jorat [a,b,*], Mark A. Goddard [b,c], Peter Manning [d], Hiu Kwan Lau [b], Samuel Ngeow [b], Saran P. Sohi [e], David A.C. Manning [b]

[a] School of Applied Sciences, Abertay University, United Kingdom
[b] School of Natural & Environmental Sciences, Newcastle University, United Kingdom
[c] Department of Geography and Environmental Sciences, Northumbria University, United Kingdom
[d] Senckenberg Biodiversity and Climate Research Centre, Frankfurt am Main, Germany
[e] School of GeoSciences, University of Edinburgh, United Kingdom

HIGHLIGHTS

- Soil carbonate in urban brownfield lands contribute to significant removal of CO_2.
- Study of 20 brownfield lands show removal rate of 4–59 t CO_2 ha^{-1} yr^{-1}.
- CO_2 sequestration rate is highest in the first 15 years after demolition.
- Sites that sequestered CO_2 possess a similar risk of flooding to sandy soils.
- Substrate strength, measured in-situ, increased with carbonation

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 June 2019
Received in revised form 30 October 2019
Accepted 15 November 2019
Available online 18 November 2019

Editor: Darrel Jenerette

Keywords:
Urban brownfield land
CO_2 removal
Carbon precipitation
Stable isotope
Permeability
Strength

ABSTRACT

Management of urban brownfield land can contribute to significant removal of atmospheric CO_2 through the development of soil carbonate minerals. However, the potential magnitude and stability of this carbon sink is poorly quantified as previous studies address a limited range of conditions and short durations. Furthermore, the suitability of carbonate-sequestering soils for construction has not been investigated. To address these issues we measured total inorganic carbon, permeability and ground strength in the top 20 cm of soil at 20 brownfield sites in northern England, between 2015 and 2017. Across all sites accumulation occurred at a rate of 1–16 t C ha^{-1} yr^{-1}, as calcite ($CaCO_3$), corresponding to removal of approximately 4–59 t CO_2 ha^{-1} yr^{-1}, with the highest rate in the first 15 years after demolition. C and O stable isotope analysis of calcite confirms the atmospheric origin of the measured inorganic carbon. Statistical modelling found that pH and the content of fine materials (combined silt and clay content) were the best predictors of the total inorganic carbon content of the samples. Measurement of permeability shows that sites with carbonated soils possess a similar risk of run-off or flooding to sandy soils. Soil strength, measured as in-situ bearing capacity, increased with carbonation. These results demonstrate that the management of urban brownfield land to retain fine material derived from concrete crushing on site following demolition will promote calcite precipitation in soils, and so offers an additional CO_2 removal mechanism, with no detrimental effect on drainage and possible improvements in strength. Given the large area of brownfield land that is available for development, the contribution of this process to CO_2 removal by urban soils needs to be recognised in CO_2 mitigation policies.

* Corresponding author at: School of Applied Sciences, Abertay University, United Kingdom.
E-mail address: e.jorat@abertay.ac.uk (M.E. Jorat).

https://doi.org/10.1016/j.scitotenv.2019.135573

1. Introduction

In the context of climate change and population growth, urbanisation presents both challenges and opportunities (Seto and Shepherd, 2009). The proportion of the global population living in cities increased from 34% (1960) to 54% (2015) and is projected to reach 66% by 2050 (United Nations, Department of Economic and Social Affairs, Population Division, 2015). Urbanisation exerts pressure on the natural environment, but cities also offer opportunities to meet global sustainable development goals as they can act as hubs for climate change adaptation and social innovation strategies (Grimm et al., 2008; McPhearson et al., 2015; United Nations, Resolution adopted by the General Assembly on 25 September 2015, 2015). One area for such innovation is in the management of urban ecosystem services, which improve the well-being of urban citizens (Bolund and Hunhammar, 1992; Perring et al., 2012; McPhearson et al., 2015). Urban lands play an essential role in delivering these ecosystem services and in minimising the negative impacts of urbanisation (Pavao-Zuckerman, 2012). In addition, urban soils play an important role in carbon capture and storage (Louwagie et al., 2016), and they have potential to augment approaches to carbon management in agricultural soils, such as the '4 per mil' initiative (Chabbi et al., 2017; Lord and Sakrabani, 2019), which was launched at the 2015 United Nations Climate Change Conference (COP 21) to reduce atmospheric CO_2 concentrations by increasing global soil organic carbon stocks by 0.4% per year.

In established urban areas, the term 'brownfield' is used for land that has previously been developed, usually for industrial or commercial purposes. Where development takes place on natural or agricultural soils, that land subsequently can be regarded as 'brownfield'. Brownfield sites typically are created through the demolition of pre-existing structures, and become vegetated through managed planting, unmanaged colonisation, or a combination of the two. Their soils commonly include Technosols (FAO, 2006), created through engineering processes. Carbon accumulation in urban soils for climate change mitigation has been the subject of research that focused on stocks of actively cycling organic carbon (e.g., Jo and McPherson, 1995; Edmondson et al., 2012, 2014; Lord and Sakrabani, 2019). However, recent studies identified a considerable and potentially greater capability for urban brownfield lands to remove CO_2 through precipitation of inorganic carbon in the form of calcite ($CaCO_3$) (Renforth et al., 2009, 2011; Washbourne et al., 2012, 2015; Manning et al., 2013; Xi et al., 2016; Jorat et al., 2017). Renforth et al. (2009) estimated an accumulation rate for total inorganic carbon (TIC) equivalent to 25 ± 12.8 t CO_2 ha^{-1} yr^{-1} at a brownfield site created in 1996, while Washbourne et al. (2015) measured a large increase in TIC over an 18 month period immediately following demolition, corresponding to removal of 85 t CO_2 ha^{-1} yr^{-1} (Washbourne et al., 2015). As these studies were conducted at single sites this paper sets out to establish whether or not accumulation of inorganic carbon occurs generally at significant rates within brownfield sites, and to identify what factors drive accumulation rates. As a first step, we focus on sites in northern England (where there is a long industrial heritage), and provide a foundation for similar studies internationally, to take into account the wide variety of brownfield site characteristics.

In order for calcite to precipitate in soil there needs to be a source of both carbonate and calcium ions (Manning and Renforth, 2013), and the availability of these sources may determine inorganic C accumulation rates. There must also be soil solution contained in pore space, where chemical reactions leading to calcite precipitation can proceed. Carbon stable isotopes (^{12}C, ^{13}C) confirm that newly formed calcite in soil has strongly negative values for $\delta^{13}C$, indicating that carbonate is derived from dissolved CO_2, that is most likely provided mainly by root respiration of photosynthetic C (Manning and Renforth, 2013), rather than remobilisation of geological carbonate (which may be present as limestone used in construction aggregates) Respiration by roots, of root-derived carbon and plant litter in soil, results in CO_2 concentrations in soil pore spaces that are greater than those in air. Sources of calcium in urban brownfield soils include fine grained demolition materials left behind by the on-site crushing and screening of concrete (Renforth et al., 2009; Washbourne et al., 2012, 2015; Manning and Renforth, 2013; Jorat et al., 2015). These materials contain the calcium-rich components of cement (portlandite, $Ca(OH)_2$, and artificial calcium silicates) and plaster (gypsum, $CaSO_4.2H_2O$). Calcium may also be derived from the weathering of natural silicate rocks such as dolerite (Manning et al., 2013), which may be used as construction aggregates depending on local availability.

Brownfield soils, or substrates, are spatially heterogeneous and diverse, reflecting often complex site histories that in industrialised regions can involve multiple phases of demolition and construction spanning 200 years or more. The texture of such soils and the size and connectivity of their pore space may vary greatly, and at a range of scales. Observation of samples from trial pits indicates that calcite precipitates onto grain surfaces and so reduces pore volume (Fig. 1). While pore space may be essential for providing a solution flow to supply the calcium and carbonate required for calcite precipitation, this porosity is diminished as carbonation proceeds, and may affect drainage in fine-grained components of the soil.

The observation that calcite precipitation takes place in urban brownfield lands provides an opportunity to adapt their management

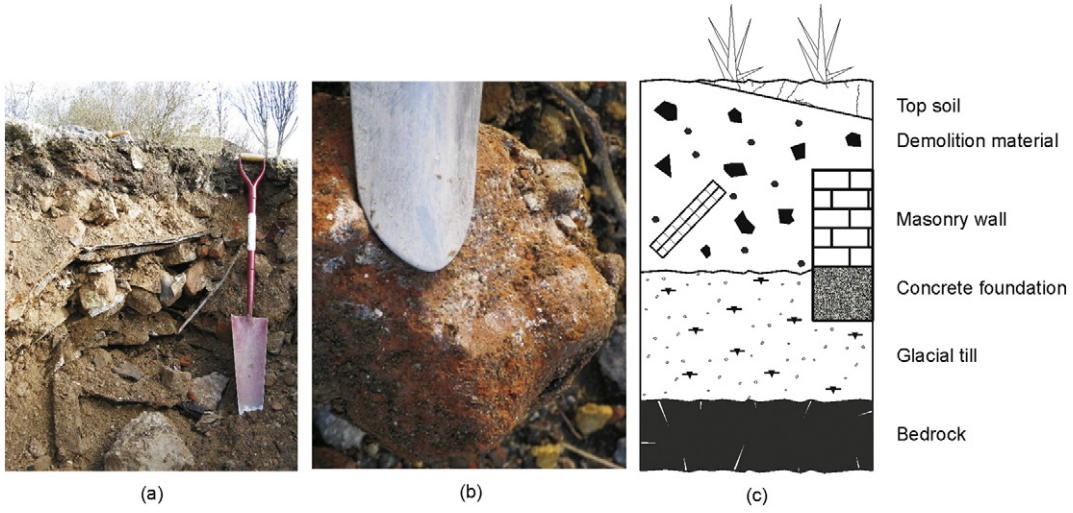


Fig. 1. Trial pit (a) from an urban brownfield site illustrating components commonly present in Technosols with (b) white minerals on the surface of a brick from the pit in (a) providing evidence of calcite precipitation and (c) typical section for Technosol in north-east England.

to promote carbonation and augment other practices which aim to remove atmospheric CO_2. A key factor is the availability of calcium, which needs to be present in sufficient quantity to enable calcite precipitation to take place. Thus, the first step in land management for this purpose is to promote soil calcium availability, such as by retention on site of fines produced by crushing concrete during demolition. An inevitable consequence of urban development, demolition is often followed by a delay before new construction, during which time the land may have a formal or informal temporary use as a green space, thus enabling photosynthetic carbon to enter the soil. Although individual sites will have specific soil characteristics, an open texture as shown in Fig. 1 is unlikely to be preserved following later construction. Nevertheless, once formed, soil carbonate minerals are stable, and do not release C back into the atmosphere. C captured in this way will remain in the solid during reworking associated with later development. Active management of brownfield sites to increase their potential for CO_2 removal (Louwagie et al., 2016) also promotes other ecosystem services (Haase et al., 2014). These principles need to be understood in the context of cities in developed, but also developing, countries where urban spread into former agricultural land will increase the rate of brownfield creation in 20–50 years, as current buildings come to their end of life.

To fully understand the future importance of calcite precipitation and its associated impacts for CO_2 removal in urban brownfield land, several questions need to be addressed.

First, it should be established whether reported carbonation rates are typical of those in brownfield soils, and by how much rates vary. Carbonation has been assessed on a small number of sites to date, where rates may not be typical.

Secondly, the duration of calcite precipitation needs to be determined, to establish whether or not the process stops after a specific period. Previous estimates of annual rates of CO_2 sequestration in brownfield sites (e.g., Renforth et al., 2009; Washbourne et al., 2012) are based on assumed intervals between demolition and soil analysis. In principle, as long as vegetation is growing, calcite precipitation will stop when either the soil calcium is exhausted, or when the pore space in which $CaCO_3$ forms is filled.

Thirdly, given that brownfield sites are heterogeneous in their soil properties and vegetation, then it is important to understand how variation in these properties relates to inorganic carbon formation. pH is a fundamental control on carbonate mineral stability. Carbonate minerals typically form in soils with pH >7.3 (Lal, 2008), and have been found to precipitate in sanitary landfills at pH as low as 5.9 (Manning and Robinson, 1999); brownfield soils can display high pH (9.5–11.7 of Washbourne et al. (2015)). Electrical conductivity reflects the soil solution solute content; for example, if gypsum is present, electrical conductivity will be relatively high. Brownfield sites also vary in the extent of vegetation cover, partly depending on the time available since demolition for plant succession to occur. Plants could play a major role in the input of carbon into the soil system by releasing CO_2 into the soil via root respiration and also through the deposition of leaf and root litter, and organic acids as root exudates, all of which are decomposed to release CO_2 into the rhizosphere. By reducing uncertainty in the rates of carbonation that can be expected, and by identifying soil factors which predict carbonation rates, carbonation through land management is more likely to be utilised and incorporated into policy.

Finally, it is possible that calcite precipitation will alter the mechanical properties of a brownfield soil, including its permeability and bearing capacity, with consequences for drainage (urban flood management) and the ability to support built structures. In unconsolidated soils, calcite precipitation can decrease porosity (Cheng et al., 2013) and reduce permeability (Song and Kwon, 2007; Jorat et al., 2015). Consequently, if pores close due to calcite precipitation, then through-drainage will be reduced, potentially leading to increased flooding in urban areas during heavy rainfall. In terms of soil mechanics, calcite precipitation can increase strength by up to 70% in experimental situations (Bertos et al., 2004). Indeed, the artificial use of Microbial Induced Calcite Precipitation (MICP) has been considered for ground improvement as it enhances strength and reduces permeability (e.g., DeJong et al., 2006; Al Qabany and Soga, 2013). All of these properties influence the capacity for carbonate-forming soils to be built upon - a likely necessity in the management of brownfield lands.

To better understand how the aforementioned factors influence rates of calcite precipitation in soil and the effect of this CO_2 removal process on soil physical properties, we collected data relating to the accumulation of calcite, soil and vegetation properties and also changes in soil structure that affect the permeability and bearing capacity of urban soils in 20 brownfield sites in north-east England. This paper expands considerably upon previous work on urban brownfield land carbonation at a single site (Washbourne et al., 2015) by studying a wider range of brownfield sites. We use statistical analysis to assess whether or not there are general predictors of carbonation rates, and to assess the relationship between carbonation and properties which may affect future building developments. The overall goal is to support decision making in urban land management that seeks to maximise CO_2 removal, while retaining other benefits (Louwagie et al., 2016).

2. Methods

In 2015, four brownfield sites in Newcastle, in 2016, 20 brownfield sites across Newcastle, Gateshead, North Shields, South Shields, Stockton-on-Tees and Hartlepool and in 2017, three brownfield sites in Newcastle were visited (Table 1). Permanent markers and mobile GPS equipment were used to ensure the accuracy of sampling in sites where repeat visits were made. Sample collection was similar to the approach used by Rawlins et al. (2008), who collected 0.5–1.0 kg to a depth of 15 cm, and by Washbourne et al. (2015) who collected 0.5–1.0 kg to 10 cm depth. In this study, a 0.5–2.5 kg soil sample to the depth of approximately 20 cm was collected from each of 10 sampling locations; samples were not pooled. Sampling locations were selected to maximise variability across gradients of soil type and vegetation and were a minimum of 20 m apart from each other. In-situ California Bearing Ratio (CBR) tests were conducted prior to the soil sampling. The collected soils consisted of demolition rubble containing fragments of building materials grading from clay-sized particles to large brick/concrete pieces of up to 5 cm.

After sampling, soils were weighed using a portable balance with the accuracy of ±5 g and stored inside a sealed plastic bag. Dry sand with known bulk density was used to fill the hole where the soil was collected. The accurate weight of the sand used to fill the hole was measured in the field. Considering the weight of the dry sand used to fill the hole and the sand's bulk density, the volume and hence bulk density of the collected soil sample can be calculated. In the laboratory, samples were air-dried, disaggregated by hand using a pestle and mortar, and sieved. For consistency, the <250 μm fraction was analysed by i2 Analytical Ltd. (Watford, UK) to determine inorganic carbon by acid digestion following BS 1377-3: 1990, and reported as equivalent calcium carbonate. This method provides a direct and unambiguous determination of carbonate carbon. Total inorganic carbon (TIC) and CO_2 equivalences were calculated stoichiometrically. Electrical conductivity was measured to elucidate the electrolyte presence within the soil solution, based upon BS7755-3.4 (1995). For electrical conductivity, 20 g dry soils were mixed with 100 mL distilled deionised water into polypropylene bottles. Samples were shaken at 180 rpm for 30 min, then passed through No. 42 filter paper into universal tubes. Electrical conductivity was measured using a Hanna HI 9835 Conductivity/TDS meter, pre-calibrated using electrical conductivity calibration solution (0.010 mol/L) potassium chloride.

Ratios of stable isotopes of C and O, expressed relative to Vienna Pee Dee Belemnite (VPDB), were determined for 73 of the soil samples collected in 2016 and 8 Carboniferous Limestone samples by Iso-Analytical (Cheshire, U.K.) using a Europa Scientific 20–20 continuous-flow

Table 1
Summary of brownfield sites surveyed across north-east England in summer 2015, 2016 and 2017. Previous use: industrial (factory/warehouse), amenity (library/school/park), residential (housing), business (offices).

Site	Sampling year	Area (km^2)	UK Ordnance Survey (OS) grid tile[a]	Approx. age (2016)	Previous use	Sampling depth (cm)	Soil description
A	2016	0.00831	NZ2563	13	Industrial	15	Mix of sand, concrete and brick pieces covered with an organic layer - trace of gravel
B	2016	0.0404	NZ4519	12	Industrial	15	
C	2016	0.0568	NZ4418	9	Industrial	15	
D	2016	0.1362	NZ4420	6	Industrial	10	
E	2016	0.0276	NZ4222	3	Amenity	15	
F	2016, 17	0.045	NZ4926	4	Industrial	5	
G	2015, 16	0.028	NZ2163	26	Industrial	15	
H	2016	0.0312	NZ2865	3	Amenity	10	Organic sandy soil overlying made ground - trace of brick and concrete pieces
I	2016	0.0976	NZ2662	14	Industrial/residential	20	
J	2015, 16	0.0335	NZ2162	26	Power station	20	
K	2016	0.0574	NZ3368	12	Industrial	15	Mix of sand, concrete and brick pieces - trace of organic soil and gravel
L	2015, 16, 17	0.0527	NZ2263	7	Residential	15	
M	2016	0.0523	NZ2460	7	Industrial	5	
N	2016, 17	0.013	NZ2264	2	Amenity	20	
O	2016	0.0667	NZ3165	27	Residential/business	5	Mix of sand, silt, clay and gravel covered with an organic layer - trace of brick and concrete pieces
P	2016	0.0256	NZ2162	12	Industrial	20	
Q	2016	0.031	NZ3368	16	Industrial	10	Mix of sand, concrete and brick pieces covered with an organic layer - trace of gravel, silt and clay
R	2016	0.0568	NZ2563	6	Housing/amenity	15	
S	2016	0.0437	NZ2262	32	Industrial	20	Mix of gravel, concrete and brick pieces covered with an organic layer - trace of sand and clay
T	2015, 16	0.0372	NZ2162	12	Industrial	15	

[a] We identified location of the sites using OS Grid tile format with 1 km^2 resolution due to frequent change of ownership of urban development sites.

isotope ratio mass spectrometer (IRMS). Four samples were submitted for each site, except for Site H for which only three were selected (79 in total; 6 analyses failed to provide isotope data), based on a range of sample TIC values. For these samples, the same material was used to determine both inorganic carbon and the C and O isotope ratios.

In-situ CBR values were obtained using a hand-driven British Military Engineering Experimental Establishment (MEXE) Cone Penetrometer. The penetrometer is pushed into the top 150 mm of soil and the value of in-situ CBR recorded (Cook et al., 2016). Three in-situ CBR readings were taken at each sampling location prior to sampling. The instrument displays the in-situ CBR immediately as the probe is being manually forced down into the ground. As this instrument is heavily dependent on the strength of the operator, tests were completed by the same person. The MEXE Probe cone penetrometer is designed specifically for fine-grained soils, and penetration was challenging when encountering hard demolition waste such as bricks and rock or masonry.

Due to the heterogeneous nature of the brownfield sites, remoulding the collected soil samples in the laboratory to represent the in-situ condition for the conventional permeability analysis (e.g., falling head or constant head permeability tests) is accompanied by a significant level of error and ultimately results in inaccurate measurement of soil permeability. As measurement of the in-situ permeability was not logistically possible, an updated version of Hazen's formula was used to estimate the hydraulic conductivity of each sample. Chapuis (2004) proposed the modified Hazen's formula as shown in Eq. (1) to calculate permeability as this formula relates the function of particle size and void ratio in coarse-grained soils:

$$K = 2.4622 \times \left(D_{10}^2 \times \frac{e^3}{(1+e)^2} \right)^{0.7825} \quad (1)$$

where e = void ratio and D_{10} = effective particle size acquired from particle size distribution curve.

Paired *t*-tests were used to determine whether there were significant changes in TIC content over time in sites sampled in consecutive years. In order to better understand the variation in carbonate precipitation within and between brownfield sites, the amount of TIC was modelled using mixed-effects statistical models according to a model selection procedure (Pinheiro and Bates, 2000). TIC and silt+clay content were log transformed to account for non-normality in variance, and an outlying data point with extremely low pH (3.5) was removed. Our model selection approach involved adding explanatory variables in fixed sequential order according to a hypothesized 'hierarchy of controls' which impact the basic processes of plant growth and organic matter (OM) decomposition and stabilization (Diaz et al., 2007; Manning et al., 2015). First, we added site age, and this was followed by the physical and chemical properties of soil that are driven mainly by site history and/or underlying parent material (soil pH, electrical conductivity, silt and clay content). Finally, we added plant cover. Variables were retained if they improved model likelihood, assessed using Akaike's Information Criterion corrected for small sample sizes (AICc), and were significant (at $p < 0.05$), assessed using likelihood ratio deletion tests (LRT). At each stage, first order interactions between significant variables were sought, as were quadratic relationships, if there was a hypothetical basis for them. At the end of each stage of model selection, interactions between newly retained variables and those retained from previous steps were sought and retained if significant. Once the final model was reached each term was removed from the model and its significance was assessed using a LRT. The modelling process indicated a negative effect of plant cover but this variable was removed from the final model as there was no hypothetical basis for a mechanistic relationship that was negative (see introduction).

To estimate the variance explained by the fixed effects of the models, we used the r.squaredGLMM function of the MuMIn package which partitions the explained variance by comparing the fit of model predictions to the data when these terms are absent from the model to calculate a 'marginal R2' (R2M). The importance of each variable in the model was also estimated by observing the AICc change (Δi) on deletion (Nakagawa and Schielzeth, 2013). All models were linear mixed-effects models with a random effect for site. Mixed models were fitted using maximum likelihood and the lmer function of the statistical software R version 3.4.1 (R Core Team 2017).

3. Results

TIC varied considerably across the sites, with mean TIC content per site ranging from 0.76–4.87% dry weight. pH varied from 7.1–8.8, silt+clay from 0.71–5.6%, electrical conductivity from 155–787 μS cm^{-1} and plant cover from 5–93% (Table S1).

The TIC content for brownfield sites visited in 2016 is shown (Fig. 2) relative to site age, and grouped at 5-year intervals (no sites occupied the interval 21–25 years). Site age refers to the time between demolition and our sampling dates. Demolition date was estimated using

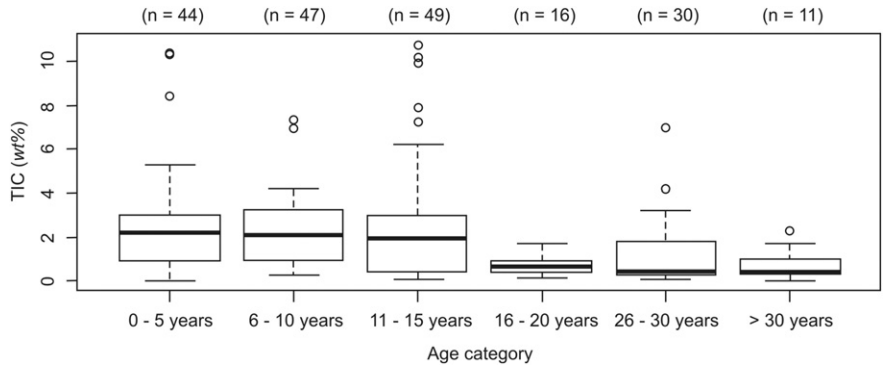


Fig. 2. Calculated TIC content (197 samples) grouped by site age in 20 brownfield sites, north-east England. Boxes show median value plus interquartile range; whiskers represent minimum and maximum values that do not exceed 1.5 x the interquartile range with points beyond this plotted as single points.

historic maps for older sites and taken from site investigation reports for newer sites. For sites younger than 15 years, median TIC values are similar at 2.2%; less than half of this was observed in sites older than 16 years. There was no significant change in soil TIC content between 2015 and 2016 across four sites that were repeatedly sampled and ranged in age between 7 and 26 years (paired *t*-test, $t = 1.375$, df = 39, $p = 0.177$). There was a significant increase in TIC for three younger sites (2–8 years since creation) between 2016 and 2017 (paired *t*-test, $t = -7.1659$, df = 29, $p < 0.001$) (Fig. 3).

The mixed-effects statistical model used to explore relationships between TIC and other soil properties accounted for 47.9% of variation in TIC ($R^2M = 28.1\%$). Log TIC was best described by a quadratic relationship with soil pH (Table 2), with TIC increasing at a decelerating rate with increasing pH over the observed range of soil pH 5.64–9.49, and peaking at a pH of 10 (Table S1). Variation in TIC was also related to the silt and clay fraction, with amounts being greatest in soil rich in silt and clay sized particles (Table 2). Site age and soil electrical conductivity were not found to be important predictors, while a negative effect of plant cover was found. This variable was removed from the final model as there was no hypothetical basis for a negative relationship.

Carbon and oxygen isotope data for the brownfield sites sampled in 2016 are shown in Fig. 4. For comparative purposes, data are included for local carbonate rocks used in construction (Carboniferous limestone and Permian carbonates, mainly dolomite; Harwood and Coleman, 1981), pedogenic carbonates from natural soils (Salomons et al., 1978; Salomons and Mook, 1976), and calcite associated with concrete structures (Macleod et al., 1991; Krishnamurthy et al., 2003) and steel slags (Renforth et al., 2009). The data for the brownfield sites clearly show overlap with those typical for pedogenic carbonates, with evidence of mixing with geological carbonate (locally derived Carboniferous limestone or Permian dolomite; note that the two Permian samples plotting with the array of pedogenic and brownfield samples are, according to Harwood and Coleman (1981) young pedogenic calcite within Permian dolomite rocks) and with carbonates associated with the chemical weathering of high pH cementitious materials. The array of data for the brownfield sites is similar in range to that reported by Washbourne et al. (2015).

Permeability varied across the sites from 0.0001–0.0502 cm s^{-1}, with most values within the range typical for sand (Fig. 5), and mean values per site ranged from 0.002 to 0.0243 cm s^{-1} (Table S2). Soils containing 0–4% TIC had 2.5 x higher permeability than those with 4–12% TIC.

In-situ soil strength, as measured as CBR, varied across the sites from 1 to 14% (Fig. 6), with mean values per site ranging from 7.70–12.86% (Table S2). In-situ CBR values were lowest in soils with low TIC content, and greatest for those with TIC>4%. These CBR values are largely within the range of typical sand in-situ (Highways England, 2009).

4. Discussion

Our investigation of 20 sites has shown that calcite commonly occurs in brownfield soils of north-east England: carbon and oxygen isotope

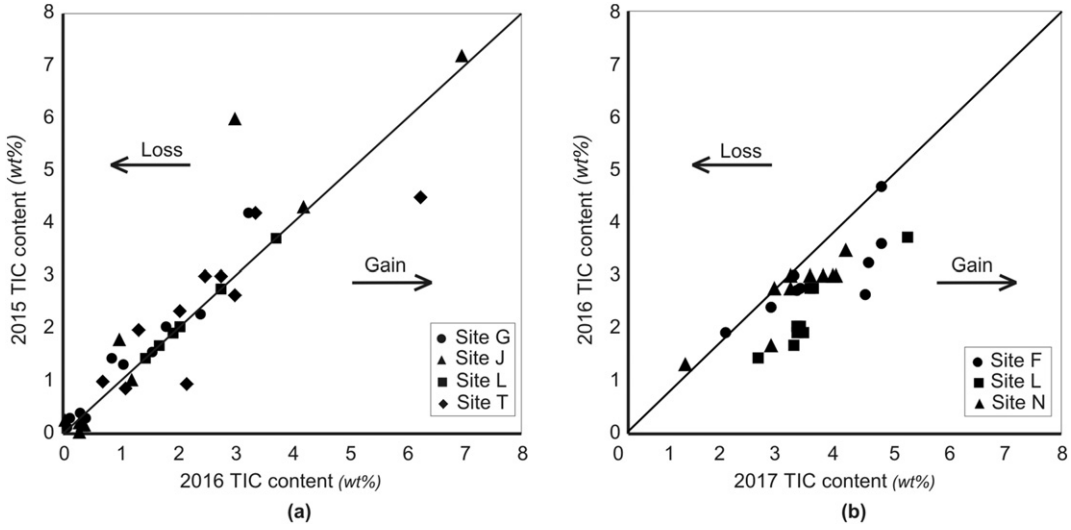


Fig. 3. Comparison of TIC concentration for sites sampled across different years (a) 2015 to 2016 (site age range 7–26 years) and (b) 2016 to 2017 (site age range 2–8 years) for brownfield sites with repeat sampling. Standard error is 0.12 wt%, Repeat analysis of a single sample approximately the size of the symbols in the plot.

Table 2
Selected best model for log TIC (wt%)[a].

Variable	Parameter estimate	AICc[b] change (Δi)[c]	p value[c]
Intercept	−4.472		
soil pH	1.001	50.26	<0.0001
(soil pH)^2	−0.050	2.38	0.0335
Log (Silt+Clay) (%)	0.228	7.79	0.0016

[a] The model was fitted to transformed data so output should be exponentiated if the model is to be used.
[b] AICc is Akaike's Information Criterion corrected for small sample sizes.
[c] Assessed with a single d.f. likelihood ratio deletion test.

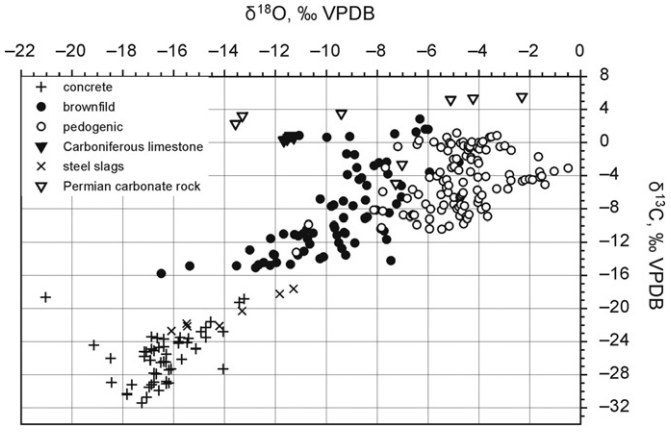


Fig. 4. Stable isotope data for samples from brownfield sites collected in 2016, with data for calcite from a range of surface environments (see text for sources). Number of samples from brownfield sites = 79.

data show unambiguously that this cannot be explained through incorporation of geological carbonate from minerals and rocks. The isotope data show values for $\delta^{18}O$, and to a lesser extent $\delta^{13}C$, that are more negative than would be expected for pedogenic carbonates, consistent with mixing between a pedogenic carbonate, in which the source of the C is via plant photosynthesis, and geological carbonates (Fig. 7). However, the data also suggest inclusion of a component characteristic of carbonation under high pH conditions, with highly negative values for both $\delta^{18}O$ and $\delta^{13}C$, as reported in studies of carbonation of concrete structures (Macleod et al., 1991; Krishnamurthy et al., 2003) and for carbonates precipitated from high pH waters associated with weathering of steel slags (Renforth et al., 2009; Mayes et al., 2018). Thus the carbonates from the brownfield sites studied here (and reported by Washbourne et al., 2015) record a history of CO_2 removal from the atmosphere through a combination of biological processes (photosynthesis) and chemical processes (carbonation at high pH), with mixing of multiple sources to give a composite sample for analysis that also includes varying amounts of limestone derived from construction aggregates.

Given that the stable isotope evidence demonstrates the formation of carbonates within the soils from the brownfield sites, in principle we can estimate the rate of their accumulation from repeated sampling, or from the age of the site. Previous attempts to estimate the accumulation rate based on site age (12 years) estimated TIC increases of 25 ± 12.8 t ha^{-1} yr^{-1}, to a depth of 300 cm, with most carbonate being found at a depth of <100 cm (Renforth et al., 2009). Washbourne et al. (2015) report an accumulation rate of 23 t C ha^{-1} yr^{-1}, for samples taken to 10 cm depth at an interval of 18 months (i.e. 36–54 months after site establishment). Based on site age and assuming zero inorganic carbon at the time of demolition, our data (for samples to 20 cm depth) for the 20 brownfield sites correspond to an accumulation of TIC of 16 t C ha^{-1} yr^{-1}, which is comparable to rates estimated by Washbourne et al. (2015), given the difference in the depth of sampling.

At the sites selected for direct measurement of annual accumulation through repeated sampling, rates (Fig. 3a) appear to be very low for sites 10 years or more since establishment, while the more recent sites in this set showed measurable increases over 12 months (Fig. 3b). Accumulation at the most recent site varied from year to year: Site L, 7 years old in 2016, showed little change between 2015 and 2016, but a measurable increase in TIC between 2016 and 2017. The observed variation for sites of different ages suggests that C did not always accumulate at the same rate either between years at the same site, or across the chronosequence. The reasons for this may include (1) mechanical migration deeper in the profile (maximum carbonate occurs in the upper 1 m of soil; Washbourne et al., 2015), or (2) older sites, for which the history is less well known, may have been less suitable for C formation than the younger ones sampled, in some unmeasured property. Interestingly, the difference in carbonate contents of sites older than 15 years (Fig. 2) may reflect introduction of the UK's Landfill Tax in 1996 and Aggregate Levy in 2002 (Martin and Scott, 2003). This led to increased recycling of construction materials (Tangtinthai et al., 2019) and it is possible that the associated widespread use of on-site crushing equipment may have led to more fine-grained crushed concrete entering the soils present at a site.

Statistical modelling considered how pH, silt+clay content and electrical conductivity and plant cover are related to TIC content. These properties were assessed as predictors of carbonate concentrations, together with site age. As might be expected on geochemical grounds, pH was found to describe variation in TIC most closely, with higher content in more alkaline soils. To a lesser extent, TIC was predicted by the

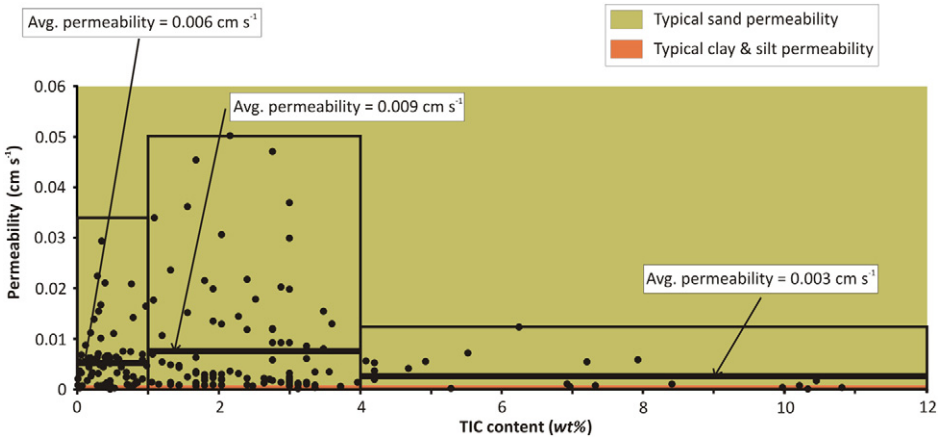


Fig. 5. Permeability of the samples collected from 2016 versus their $CaCO_3$ content. Standard error for permeability is 0.007 cm s^{-1} and TIC is 0.12%, approximately the size of the symbol in the plot. Typical permeability values are those of Lewis et al. (2006). Number of samples = 182.

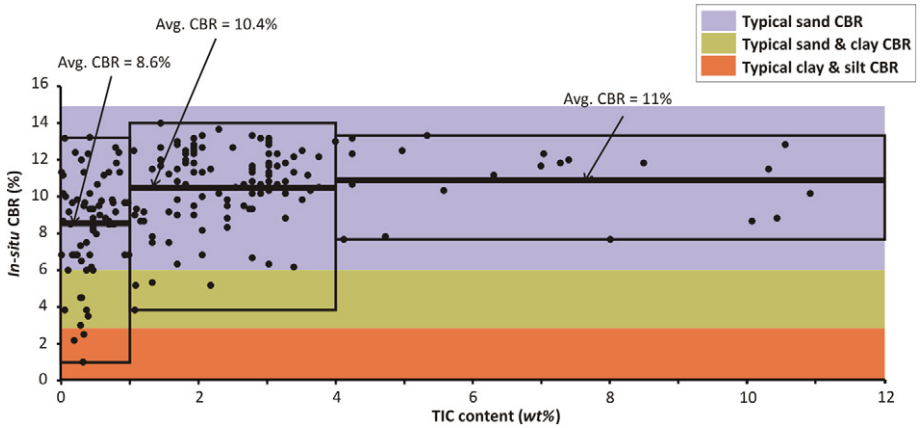


Fig. 6. In-situ CBR of the samples collected from 2016 versus their $CaCO_3$ content. Standard error for CBR is 1.2% and 0.12% for TIC, approximately the size of the symbol in the plot. In-situ CBR values derived from Highways England (2009). Number of samples = 189.

content of fine material (combined silt and clay content), suggesting that calcite precipitation is greatest in fine-grained soils. This is likely to be due to their greater surface area for reaction. Although TIC accumulation was measurable in younger sites, neither electrical conductivity nor site age were found to be significant predictors of TIC content in the model. Electrical conductivity may be highly variable within a soil of this type, depending on the presence of relatively soluble components such as gypsum or portlandite. The observed high variability may simply reflect very local (within sample) and within-site variability (between the 10 samples) heterogeneity in mineralogical composition (Table S1). Plant cover was negatively related to soil TIC, possibly reflecting a relationship with an unmeasured driver of TIC that also affected plant growth and survival, such as high pH. While the negative relationship between pH and plant cover at the sampling plot scale (Spearman's rank correlation, $r_s = -0.60$, n = 370, $p < 0.0001$) was accounted for statistically, it does not account for relationships with unmeasured soil chemical properties.

While it is clear from stable isotope data that newly formed carbonate minerals occur within the urban brownfield soils of this study, providing evidence of the existence of a carbon capture process, the consequences for other urban soil services (e.g., drainage, load-bearing capacity) need to be considered. The geotechnical property of permeability varies with TIC content. Average permeability was lowest for samples with the highest TIC content (Fig. 5), but still lies with the range expected for sand, i.e., >0.001 cm s^{-1}. Thus, sites in which carbonation has taken place appear not to be at greater risk of run-off or flooding than any other sandy soil. Permeability was not reduced to the low levels typical of soils associated with flooding, such as those developed on glacial till ($6 \times 10^{-4} < k < 1 \times 10^{-10}$ cm s^{-1}; Lewis et al., 2006). Strength was also related to TIC; low CBR values did not occur in locations where soil samples contained >4% TIC. This suggests that carbonation improves soil strength, consistent with the use of MICP to achieve this artificially (DeJong et al., 2006; Al Qabany and Soga, 2013; Montoya and DeJong, 2015).

Given the wide occurrence of soil carbonation that was observed, this study confirms that urban brownfield lands can be an important tool for CO_2 removal. On the basis of our measurements for 20 brownfield sites, the estimated maximum TIC accumulation rates in the top 20 cm of soil, corresponding to the root zone for a wide range of amenity plants, is 16 t C ha^{-1} yr^{-1}, which corresponds to removal of approximately 59 t CO_2 ha^{-1} yr^{-1}. While these values are lower than those estimated from previous single site studies and sample depth ranges, they are still very high in comparison to rates of organic carbon sequestration; the rate of accumulation of soil organic carbon in forest is at most 0.3 t C ha^{-1} yr^{-1} (Jandl et al., 2007). When brownfield lands containing carbonated soil are redeveloped and soil is sealed by impermeable structures, sequestered CO_2 remains as a stable sink in soil as the mineral calcite, $CaCO_3$.

In detail, the interpretation of carbon accumulation rates over time is complicated by the small size and shallow depth of the samples taken for analysis. In previous work, it has been shown from trial pits to <300 cm depth that brownfield sites typically show elevated inorganic C to depths of 100 cm (Renforth et al., 2009; Washbourne et al., 2015). Thus, accumulation rates should ideally be based on sampling to 100 cm depth, and in brownfield sites, this usually can only be achieved by trial pitting with a mechanical excavator, given soil heterogeneity (Fig. 1). We attempted in this study to investigate a wide range of sites, using near-surface soil samples that could be taken using hand tools. The apparent association with particle size shown by the statistical model, combined with observations from other studies, suggests that migration of carbonate solids takes place through the profile, and so our measurements have not recorded the true carbon accumulation rates for each site. This explains the data presented in Figs. 2 and 3, which do not show the clear trend with age reported by Washbourne et al. (2015), and accumulation rates are likely to have been underestimated. Accurate determination of soil carbonation in brownfield sites could be achieved by routinely including TIC as a determinant in the suite of elements sought by commercial laboratories in ground investigations that involve trial pits or similar intrusive sampling.

Our results indicate that the retention of crushed demolition waste on site, and/or the addition of new crushed material to sites (e.g., incorporating demolition waste or crushed basic rocks within the landscaping of new urban infrastructure developments), may strongly promote carbon capture. To place this in the context of CO_2 removal on a larger scale, relevant to national targets, and based on an accumulation rate of 16 t C ha^{-1} yr^{-1}, management of 50,000 ha of urban soils to 20 cm depth has the potential to remove 3 Mt CO_2 yr^{-1} from the atmosphere, simply as a consequence of carbonation of concrete generated by on-site demolition. The UK has a target to reduce its greenhouse gas emissions from 379 Mt CO_2e in 2016 (Department for Business, Energy, and Industrial Strategy, 2016) to 159 Mt CO_2e in 2050 (Fankhauser et al., 2009). With 400,000 ha urban land (including connecting infrastructure), and 1,365,500 ha suburban land (Rowland et al., 2017), we estimate that management of 1% of this total stock (i.e. 17,655 ha), by providing a source of calcium in the form of crushed concrete or other sources, would remove 1 Mt CO_2 annually. Our results suggest that the process would continue for up to 15 years (Fig. 2), potentially giving a total of 15 Mt CO_2 removal, much of which is removed to deeper in the soil profile, thus accounting for the high TIC values observed in historical sites for the top metre (Renforth et al., 2009; Washbourne et al., 2015). Thus, appropriate management of just 10% of the UK's urban/suburban land stock could meet 5% of the required

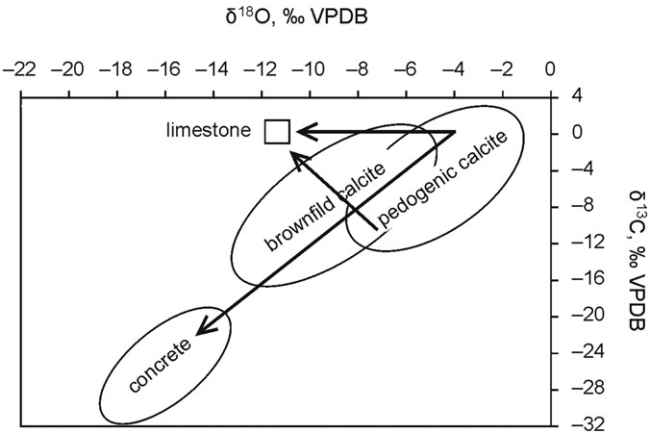


Fig. 7. Simplified diagram to show the mixing of different components to give observed C and O stable isotope ratios.

reduction in CO_2 emissions, Similarly, Western Europe has 13 M ha of urban land, increasing at a rate of 4.5% yr^{-1} (Romano and Zullo, 2013). Managing the area of growth alone (initially 600,000 ha), e.g., by adding crushed concrete or other calcium silicates prior to construction, has the potential to remove ~35 Mt CO_2 annually. This is 12% of the anticipated CO_2 emission target in 2050 recommended by Meyer-Ohlendorf et al. (2018). Beyond Europe, the USA has around 28 million ha urban land (www.census.gov), again offering abundant scope for CO_2 removal through appropriate land management.

5. Conclusions

This study of 20 urban brownfield sites has shown unambiguously, based on C and O isotope analysis, that carbonate minerals have formed as a consequence of reaction between the soil and atmospheric CO_2. The rate of carbonate mineral accumulation corresponds to an increase in inorganic carbon in the top 20 cm of the soil of 16 t C ha^{-1} yr^{-1}, similar to rates observed in other studies. However, the observed rates varied greatly, and in some case could not be determined in repeated sampling. We conclude that this relates to our experimental design, which does not account for migration of carbonate minerals to greater depths in the soil profile. Although the data show considerable scatter, we find no evidence that soil carbonation reduces permeability to increase the risk of flooding, and overall we observed an increase in soil bearing capacity with increased carbonation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We acknowledge financial support from the Engineering and Physical Sciences Research Council (EP/K034952/1) and the Natural Environmental Research Council (Greenhouse Gas Removal NE/P019501/1). We thank Kevin Stott and Chris Teasdale for their assistance in the field and in processing samples. We are grateful to Gateshead City Council, Newcastle City Council, Stockton-on-Tees Borough Council, Hartlepool Borough Council, South Tyneside Council, North Tyneside Council, the Newcastle Upon Tyne Hospitals NHS Foundation Trust, and other private landowners for assisting with access to sites. We thank two reviewers for their comments, which have improved the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.135573.

References

Al Qabany, A., Soga, K., 2013. Effect of chemical treatment used in MICP on engineering properties of cemented soils. Géotechnique 63 (4), 331–339.
Bertos, M.F., Simons, S.J.R., Hills, C.D., Carey, P.J., 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2. J. Hazard. Mater. B112, 193–205.
Bolund, P., Hunhammar, S., 1992. Ecosystem services in urban areas. Ecol. Econ. 29 (2), 293–301.
Chabbi, A., Lehmann, J., Cisis, P., Loescher, H.W., Cotrufo, M.F., Don, A., SanClements, M., Schipper, L., Six, J., Smith, P., Rumperl, C., 2017. Aligning agriculture and climate policy. Nat. Clim. Chang. 7 (5), 307–309.
Chapuis, R.P., 2004. Predicting the saturated hydraulic conductivity of sand and gravel using effective diameter and void ratio. Can. Geotech. J. 41 (5), 787–795.
Cheng, L., Cord-Ruwisch, R., Shahin, M.A., 2013. Cementation of sand soil by microbially induced calcite precipitation at various degrees of saturation. Can. Geotech. J. 50 (1), 81–90.
Cook, J., Dobie, M., Blackman, D., 2016. The development of APT methodology in the application and derivation of geosynthetic benefits in roadway design. In: Aguiar-Moya, J., Vargas-Nordcbeck, A., Leiva-Villacorta, F., Loría-Salazar, L. (Eds.), The Roles of Accelerated Pavement Testing in Pavement Sustainability. Springer, Cham, pp. 257–275.
DeJong, J.T., Fritzges, M.B., Nusslein, K., 2006. Microbially induced cementation to control sand response to undrained shear. J. Geotech. Geoenviron. Engng. 132 (11), 1381–1392.
Department for Business, Energy & Industrial Strategy, 2016. UK Greenhouse Gas Emissions. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/679334/2016_Final_Emissions_Statistics_one_page_summary.pdf.
Diaz, S., Lavorel, S., de Bello, F., Quetier, F., Grigulis, K., Robson, T.M., 2007. Incorporating plant functional diversity effects in ecosystem service assessments. Proc. Natl. Acad. Sci. U. S. A. 104, 20684–20689.
Edmondson, J.L., Davies, Z.G., McHugh, N., Gaston, K.J., Leake, J.R., 2012. Organic carbon hidden in urban ecosystems. Sci. Rep. 2 (963), 1–7.
Edmondson, J.L., Davies, Z.G., McCormack, S.A., Gaston, K.J., Leake, J.R., 2014. Land-cover effects on soil organic carbon stocks in a European city. Science of Total Environment 472, 444–453.
Fankhauser, S., Kennedy, D., Skea, J., 2009. The UK's carbon targets for 2020 and the role of the committee on climate change. In: Giddens, A., Latham, S., Liddle, R. (Eds.), Building a Low-carbon Future the Politics of Climate Change. Policy Network, London, pp. 100–111.
FAO (Food and Agriculture Organization of the United Nations), 2006. World reference base for soil resources 2006: a framework for international classification, correlation and communication. World Soil Resource Reports, Rome (145p).
Grimm, N.B., Faeth, S.H., Golubiewski, N.E., Redman, C.L., Wu, J.G., Bai, X.M., Briggs, J.M., 2008. Global change and the ecology of cities. Science 319, 756–760.
Haase, D., Hasse, A., Rink, D., 2014. Conceptualizing the nexus between urban shrinkage and ecosystem services. Landsc. Urban Plan. 132, 159–169.
Harwood, G.M., Coleman, M.L., 1981. Isotopic evidence for UK Upper Permian mineralization by bacterial reduction of evaporites. Nature 301, 597–599.
Highways England, 2009. Interim Advice Note 73/06(W) Revision 1: Design Guidance for Road Pavement Foundations (Draft HD25) (59p).
Jandl, R., Lindner, M., Vesterdal, L., Bauwens, B., Baritz, R., Hagedorn, F., Johnson, D.W., Minkkinen, K., Byrne, K.A., 2007. How strongly can forest management influence soil carbon sequestration? Geoderma 137, 253–268.
Jo, H.K., McPherson, G.E., 1995. Carbon storage and flux in urban residential greenspace. J. Environ. Manag. 45 (2), 109–133.
Jorat, M.E., Kolosz, B.W., Sohi, S., Lopez-Capel, E., Manning, D.A.C., 2015. Changes in geotechnical properties of urban soils during carbonation. 15th Pan-American Conference on Soil Mechanics and Geotechnical Engineering, 2015, Buenos Ares, Argentina, pp. 912–918.
Jorat, M.E., Kolosz, B.W., Goddard, M.A., Sohi, S.P., Akgun, N., Dissanayake, D., Manning, D.A.C., 2017. Geotechnical requirements for capturing CO_2 through highways land. International Journal of GEOMATE 13 (35), 22–27.
Krishnamurthy, R.V., Schmitt, D., Atekwana, E.A., Baskaran, M., 2003. Isotopic investigations of carbonate growth on concrete structures. Appl. Geochem. 18, 435–444.
Lal, R., 2008. Carbon sequestration. Philos. Trans. R. Soc. B Biol. Sci. 363 (1492), 815–830.
Lewis, M.A., Cheney, C.S., Ódochartaigh, B., 2006. Guide to permeability indices. British Geological Survey Open Report (CR/06/160N, 29p).
Lord, R., Sakrabani, R., 2019. Ten-year legacy of organic carbon in non-agricultural (brownfield) soils restored using green waste compost exceeds 4 per mille per annum: benefits and trade-offs of a circular economy approach. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2019.05.174 in press.
Louwagie, G., Morris, J., Kibblewhite, M., 2016. Soil resource efficiency in urbanised areas. Analytical framework and implications for governance. EEA Report no 7/2016. https://doi.org/10.2800/020840 Luxembourg, 94p.
Manning, D.A.C., Renforth, P., 2013. Passive sequestration of atmospheric CO_2 through coupled plant-mineral reactions in urban soils. Environmental Science & Technology 47, 135–141.

Manning, D.A.C., Robinson, N., 1999. Leachate-mineral reactions: implications for drainage system stability and clogging. 7th Internat. Waste Management & Landfill Symposium, Sardinia, pp. 269–276.
Manning, D.A.C., Renforth, P., Lopez-Capel, E., Robertson, S., Ghazireh, N., 2013. Carbonate precipitation in artificial soils produced from basaltic quarry fines and composts: an opportunity for passive carbon sequestration. International Journal of Greenhouse Gas Control 17, 309–317.
Manning, P., de Vries, F.T., Tallowin, J.R.B., et al., 2015. Simple measures of climate, soil properties and plant traits predict national-scale grassland soil carbon stocks. J. Appl. Ecol. 52, 1188–1196.
Martin, A., Scott, I., 2003. The effectiveness of the UK landfill tax. J. Environ. Plan. Manag. 46, 673–689.
Mayes, W.M., Riley, A.L., Gomes, H.I., Brabham, P., Hamlyn, J., Pullin, H., Renforth, P., 2018. Atmospheric CO_2 sequestration in iron and steel slag: Consett, Co. Durham, UK. Environ. Sci. Technol 52, 7892. https://doi.org/10.1021/acs.est.8b01883.
McPhearson, T., Andersson, E., Elmqvist, T., Frantzeskaki, N., 2015. Resilience of and through urban ecosystem services. Ecosystem Services 12, 152–156.
Meyer-Ohlendorf, N., Voß, P., Velten, E., Görlach, B., 2018. EU greenhouse gas emission budget: implications for EU climate policies. What Does 2050 Mean for 2030? (41p).
Montoya, B.M., DeJong, J.T., 2015. Stress-strain behavior of sands cemented by microbially induced calcite precipitation. J. Geotech. Geoenviron. Engng. 141 (6), 04015019.
Nakagawa, S., Schielzeth, H., 2013. A general and simple method for obtaining R^2 from generalized linear mixed-effects models. Methods Ecol. Evol. 4, 133–142.
Pavao-Zuckerman, M.A., 2012. Urbanization, soils and ecosystem services. In: Wall, D.H. (Ed.), Soil Ecology and Ecosystem Services. Oxford University Press, Oxford, pp. 270–278.
Perring, M.P., Manning, P., Hobbs, R.J., Lugo, A.E., Ramalho, C.E., Standish, R.J., 2012. Novel urban ecosystems and ecosystem services. In: Hobbs, R.J., Higgs, E.S., Hall, C.M. (Eds.), Novel Ecosystems. John Wiley & Sons, Ltd, pp. 310–325.
Pinheiro, J.C., Bates, D.M., 2000. Mixed-effects Models in S and S-PLUS. Springer-Verlag, New York.
Rawlins, B.G., Vane, C.H., Kim, A.W., Tye, A.M., Kemp, S.J., Bellamy, P.H., 2008. Methods for estimating types of soil organic carbon and their application to surveys of UK urban areas. Soil Use Manag. 24, 47–59.
Renforth, P., Manning, D.A.C., Lopez-Capel, E., 2009. Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide. Appl. Geochem. 24, 1757–1764.
Renforth, P., Leake, J.R., Edmondson, J., Manning, D.A.C., Gaston, K.J., 2011. Designing a carbon capture function into urban soils. Proceedings of the ICE-Urban Design and Planning 164 (2), 121–128.
Romano, B., Zullo, F., 2013. Models of urban land use in Europe: assessment tools and criticalities. International Journal of Agricultural and Environmental Information Systems 4, 80–97.
Rowland, C.S., Morton, R.D., Carrasco, L., McShane, G., O'Neil, A.W., Wood, C.M., 2017. Land Cover Map 2015 (25m Raster, GB). NERC Environmental Information Data Centre https://doi.org/10.5285/bb15e200-9349-403c-bda9-b430093807c7.
Seto, K.C., Shepherd, J.M., 2009. Global urban land-use trends and climate impacts. Curr. Opin. Environ. Sustain. 1 (1), 89–95.
Song, H.-W., Kwon, S.-J., 2007. Permeability characteristics of carbonated concrete considering capillary pore structure. Cem. Concr. Res. 37 (6), 909–915.
Tangtinthai, N., Heidrich, O., Manning, D.A.C., 2019. Role of policy in managing mined resources for construction in Europe and emerging economies. J. Environ. Manag. 236, 613–621.
United Nations, Department of Economic and Social Affairs, Population Division, 2015. World Urbanization Prospects: The 2014 Revision, (ST/ESA/SER.A/366). Available from. https://esa.un.org/unpd/wup/Publications/Files/WUP2014-Report.pdf.
United Nations, Resolution adopted by the General Assembly on 25 September 2015, 2015. Transforming our world: the 2030 agenda for sustainable development. Available from. http://www.un.org/sustainabledevelopment/sustainable-development-goals/.
Washbourne, C.L., Renforth, P., Manning, D.A.C., 2012. Investigating carbonate formation in urban soils as a method for capture and storage of atmospheric carbon. Sci. Total Environ. 431, 166–175.
Washbourne, C.L., Lopez-Capel, E., Renforth, P., Ascough, P.L., Manning, D.A.C., 2015. Rapid removal of atmospheric CO_2 by urban soils. Environmental Science & Technology 49 (9), 5434–5440.
Xi, F., Davis, S.J., Ciais, P., Crawford-Brown, D., Guan, D., Pade, C., Shi, T., Syddall, M., Lv, J., Ji, L., Bing, L., Wang, J., Wei, W., Yang, K.H., Lagerblad, B., Galan, I., Andrade, C., Zhang, Y., Liu, Z., 2016. Substantial global carbon uptake by cement carbonation. Nat. Geosci. 9, 880–883.